

## DEVOLATILIZATION, A MOLECULAR MODELING APPROACH

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### Abstract

Simulated devolatilization of in-house generated molecular models, which are representative of both the chemical and physical structures of bituminous coals, provides a unique insight into bond breaking and bond reforming mechanisms. A series of molecular models for rapidly heated bituminous vitrinites chars is presented. It was necessary to include bond formation in addition to bond breaking reactions to simulate the devolatilization process. Strong bond cleavage, sometimes prior to weak bond cleavage, was important for structural transitions. Structural units attached to the vitrinite/vitrinite-char matrix with two or fewer bonds contributed the bulk of the mass loss. However, bond-forming reactions also incorporate such structures into the char matrix, thereby reducing their probability of release. Internal hydrogen redistribution is responsible for the extent of molecular orientation in these bituminous vitrinite chars.

### Introduction

There have been a number of different models proposed for the devolatilization (pyrolysis) process. Unfortunately, even with a relatively complete chemical structure, the pyrolysis behavior of coals can not be predicted *a priori*. Some of the devolatilization models rely on network models while others employ structural or functional group models (1-5). All the devolatilization models are simplistic with regard to coal structure and none incorporate physical properties. Realistic molecular models would be of considerable aid in following and understanding the devolatilization process. It is well recognized that the maceral groups found in coal are chemically and physically distinct over most of the rank range (6) and thus behave differently during devolatilization. A significant reduction in the complexity of devolatilization is achieved here by considering only the vitrinite maceral group, specifically telocollinite obtained from *Sigillaria* tree remains.

### Experimental

Pure vitrinites (purity obtained from microscopic evaluations) were obtained from obvious tree remains in the roofs of the Upper Freeport and Lewiston-Stockton coal seams. Narrow size fractions were obtained by wet sieving. The 200x400 mesh (US Standard Sieve) cut was analyzed by a combination of chemical ( $^{13}\text{C}$  CPMAS,  $^1\text{H}$  CRAMPS NMR, flash-pyrolysis gc-ms, proximate and ultimate analyses) and physical techniques (surface area, helium density, particle size, and shape). Molecular structures of the vitrinites were generated using the SIGNATURE program (7, 8) and their physical evaluation made using one of its components (9). Molecular structures of the chars were made by manipulation (devolatilization) of the vitrinite structures. The chemical and physical evaluation of the chars models being performed by the SIGNATURE program and its components.

Vitrinite-chars were produced by rapid heating ( $10^5\text{ }^\circ\text{s}^{-1}$ ) in a nitrogen atmosphere in a drop-tube reactor operating at a temperature of  $1,400\text{ }^\circ\text{C}$ . The chars were collected at different positions to represent the transition from vitrinite to devolatilized char. Tar was removed by THF solvent extraction, and NMR samples were treated with Sml, to remove free radicals and improve the quantitative nature of the NMR experiments. A portion of the samples were demineralized prior to certain characterizations. Otherwise the chars were analyzed in a manner similar to the vitrinites.

### Results and Discussion

Structural characteristics of the vitrinites and vitrinite-chars are presented in Table 1. The vitrinites, although similar in bulk characteristics, differ in the fine structure and devolatilization behavior. The elemental compositions of the vitrinite and vitrinite-chars are presented in Table 2. Despite having different initial fine structures, the devolatilized char structures are chemically similar but physically different. Helium densities of dry, demineralized samples were 2.04 and  $1.34\text{ g/cm}^3$  (ash-free basis), BET surface areas were  $11.2$  and  $0.5\text{ m}^2/\text{g}$ , and particle swelling factors of 2.5 and 1.8 were obtained by laser light scattering for the UF and LS vitrinite-chars, respectively.

Devolatilization was performed manually on the vitrinite models, initially according to devolatilization "rules". Initially, this was a simple bond-breaking process based solely on bond strength. However, using this weakest-first approach resulted in a structure that was too aromatic, and did not yield the required mass loss. It was also evident that a large concentration of free radicals was present. Radical recombination of multiple radical pairs resulted in a very dense and strained char. This indicated that the pyrolysis process could not be considered solely as a bond breaking process, but rather as a combined bond breaking and bond forming process. Thus, the initial rationale for the computational devolatilization was found to be in considerable error.

The question that arises is "under what conditions will stronger bonds break before or around the same time as weaker bonds?". There are two extremes for bond breaking: infinite time with infinitesimal temperature rise, and rapid heating. Under infinite time with infinitesimal temperature rise the bonds will be broken in order of bond strengths. Where the temperature rise is rapid, there is energy available to break stronger bonds before all weaker bonds have had an opportunity to undergo homolytic bond cleavage. Assuming that at any point in time a structural unit (hydroaromatic or aromatic units) is more likely to have two bonds broken than three (or even

four), then those structures will contribute to the volatile fraction preferentially. However, this does not necessarily indicate that the vitrinite contains structures that are predetermined to be volatiles. Pyrolysis is a bond breaking and bond forming process, those structures initially bonded once or twice to the char matrix can be incorporated into the char matrix in such a manner as to inhibit release. Conversely, loss of a structural unit to the volatile fraction with proton radical capping of the bonding site can create structural units that can then be preferentially lost to the volatile fraction. This bond breaking, bond forming approach was used to generate the initial char structure from the 13 cm. sampling location (estimated particle temperature range of 650-950 °C, 0.06-0.15 s residence time and estimated mass loss of 20%). This mass loss approach appears to be valid in that, despite losing one fifth of the mass, the constitution of both vitrinites has changed little (Table 1). This was expected as it has been shown that the initial tar structure is chemically similar to the parent coal under rapid-heating pyrolysis conditions (10).

Preferential removal of units attached to the char matrix two or fewer times was used to generate the 23 cm. char models (1,090-1,400 °C particle temperature range and 0.15-0.33 s residence time). Again reasonable mass losses of 26 and 40 % were obtained for the UF and LS vitrinites, respectively. However, the atomic H/C ratios were too high and the carbon aromaticities of the chars too low. Thus, double bonds were introduced into the structure by hydrogen abstraction from aliphatic chains, creating two  $sp^2$  hybridized carbons (which are included in the aromaticity values) or aromatization of hydroaromatic structures. Some of the hydrogen radicals formed were redistributed to terminate free radicals. This supply of hydrogen is instrumental in allowing thermoplasticity in the char with the resulting macroscopic flow and cenosphere formation. It has been suggested that a supply of hydroaromatic hydrogen is necessary for thermoplastic behavior (11). However, in addition to hydroaromatic hydrogen, for this coal structure a considerable quantity of hydrogen can be obtained from the  $sp^2$  hybridization of short chain aliphatics (approximately C2-C3) that appear to be a component of the vitrinite structure, presumably from their presence in the parent lignin. This step also results in a structure where rapid and substantial loss of hydrogen with aromatic sheet growth can occur.

In the transition in the char structure from the 23 to the 33 cm. sampling location, the model mass loss was partially achieved by removing units attached to the char matrix two or fewer times. The remaining hydroaromatics underwent aromatization, and aliphatics were incorporated into the aromatic structures or were removed as methane or acetylene. The remaining oxygen in the char was assumed to be emitted only as CO, as it was well dispersed throughout the char model. Removal of a substantial quantity of hydrogen was necessary to achieve the appropriate H/C ratios (Table 2). This was achieved by hydrogen-carbon bond cleavage and subsequent radical-radical recombination or radical propagation with hydrogen radical expulsion. This hydrogen removal often increased the size of the aromatic units and because of the linear cantanation of the aromatic structures, generally resulted in preferential alignment of the aromatic units.

Pentagon ring formation from aromatic unit combination and from carbazole and fluorine structures resulted in curvature of the aromatic sheet. Seven membered ring structures are also created when chair and zig-zag configurations combine. This curvature prevents efficient stacking of the aromatic sheets and prevents graphitic formation. It may also be responsible for closed microporosity and hence a lower helium density. However, helium density values for the LS 33 cm. char model were considerably higher than the experimental value, 1.85 and 1.34 g/cc, respectively. Typical densities of chars generated by a slow heating rate (North American coals) are between 1.7 and 2.1 g/cc on an ash free basis. These values are consistent with the predicted char model density (1.85 g/cc). Given the constraints of the chemical evaluations, an experimental helium density value similar to that of a raw bituminous coal must be due to closed porosity.

A representation of the structural transitions for the LS vitrinite to char structures at the sampling locations of 13, 23 and 33 cm. is shown in Figure 1. The structures are in reasonable agreement with both mass loss and bulk composition and chemical structure.

## Conclusions

Molecular models representative of telocollinite from the Upper Freeport and Lewiston-Stockton coal seams have been generated and subjected to simulated, rapid-heating devolatilization. Molecular models that are in reasonable agreement with the mass loss and chemical structural features of drop-tube reactor generated chars have been produced by following simple devolatilization rules. The bulk of the mass loss can be accounted for by structural units attached to the coal/char matrix by two or fewer bonds. However, the bond formation process may incorporate such structures into the char matrix in a manner that would preclude release, i.e. pyrolysis is a bond forming and bond breaking process. Strong bond rupture can occur at the same time as, or prior to, weak bond rupture. The changes in the carbon and proton aromaticities can be achieved by some hydroaromatization of hydroaromatic units but also by  $sp^2$  hybridization of aliphatic carbons.

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**Table 1**  
Chemical Data for UF and LS Vitrinite and Chars

Sample	$f_a$	$H_a$	CH3	H/C	H/Cali	H/Cali*
UF Vitrinite	0.79	0.45	0.08	0.76	1.9	1.2
13	0.83	0.51	0.06	0.73	2.1	1.6
23	0.87	0.44	0.07	0.64	2.1	1.5
33	1.00			0.24		
LS Vitrinite	0.82	0.45	0.05	0.78	2.4	2.2
13	0.86	0.47	0.05	0.75	2.4	2.2
23	0.87	0.58	0.04	0.68	1.7	1.2
33	0.99		0.00	0.21	0.0	0.0

$f_a$  is the aromaticity,  $H_a$  is the proton aromaticity, H/C is the atomic hydrogen to carbon ratio, H/Cali is the aliphatic atomic hydrogen to carbon ratio, H/Cali\* is the non-methyl aliphatic atomic hydrogen to carbon ratio.

**Table 2**  
Elemental Composition of UF and LS Vitrinite and Chars

Sample	No of C	No of H	No of N	No of O
UF Vitrinite	100	75.5	1.2	4.4
13	100	72.8	1.2	6.5
23	100	63.5	1.8	7.9
33	100	24.4	2.9	0.8
43	100	8.8	1.4	0.0
LS Vitrinite	100	77.9	1.4	6.3
13	100	75.3	1.4	4.2
23	100	68.0	1.4	6.2
33	100	20.7	1.6	0.2

Data presented are normalized to 100 carbon atoms, oxygen was calculated using the weight % obtained by difference.

Figure 1. Structural Transitions of the LS Vitrinite to Char. (The initial structure is the LS Vitrinite, followed by the 13 , 23 and 33 cm. char models)

